



Natural, cheap and environmentally friendly binder for supercapacitors

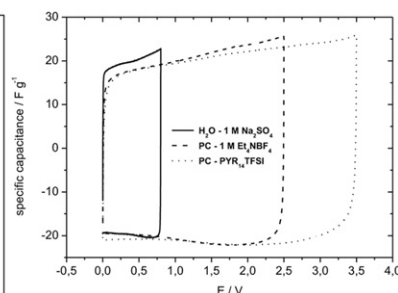
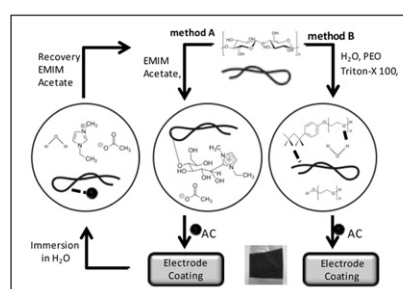
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HIGHLIGHTS

- Natural cellulose can be used as binder in supercapacitors.
- Cellulose-based electrodes display thermal stabilities comparable to those of conventional electrodes.
- Cellulose-based electrodes can be successfully used in all type of electrolytes.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work we report the use of natural cellulose as the binder for composite electrodes for electrochemical double-layer capacitors (EDLCs). Composite electrodes containing natural cellulose as the binder can be prepared using either ionic liquid based slurries or aqueous suspensions containing a polymeric stabilizer and a surfactant. These composite electrodes display good mechanical stability, uniform morphology and a thermal stability comparable to those made with conventional binders. Moreover, when used as electrodes in EDLCs, they allow the realization of devices able to display high performance in term of specific capacitance and cycling stability in all type of electrolytes used in EDLCs. Considering the appealing properties of natural cellulose, the introduction of this material as a binder in EDLCs could be an important contribution for the development of cheap, safe and environmentally friendly EDLCs.

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1. Introduction

Electrochemical double-layer capacitors (EDLCs), also known as supercapacitors, are today considered one of the most important energy storage devices [1,2]. In EDLCs the charge is electrostatically stored at the electrode–electrolyte interface and, because of this storage mechanism, these devices can be charged and discharged within seconds. The commercial available EDLCs display high power (up to 10 kW kg^{−1}) and extremely high cycle life (>500,000). These characteristics are conveniently used in a large number of applications where rapid charge–discharge capability and reliability are required [3,4].

In the last years many efforts have been made to improve the performance of EDLCs [1–3], considerably work focused on the development of carbonaceous materials with high specific capacitance [5,6]. At the same time, new types of electrolytes (e.g. ionic liquids) have been proposed with the aim to increase the operative voltage of these devices [7–9]. The results of these studies gave valuable information about the materials and the strategies which can be used for the realization of high performance EDLCs. However, only few studies focused on the inactive components of EDLCs, e.g. conductive agent and binder, although these materials are necessary for the device fabrication, and they might strongly affect the performance as well as the overall safety and the environmental friendliness of EDLCs [10].

So far, fluorinated thermoplastics binders, such as polytetrafluoroethylene (PTFE) and polyvinylidene difluoride (PVdF), have

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been widely used and represent the state-of-the-art binders in EDLCs [11]. Recently, few studies also reported about the use of derivatives of those two binders, e.g. PVdF-hexafluoropropylene (PVdF-HFP) [12] and Nafion [13,14], a perfluorosulfonated ionomer derived from PTFE. These binders can be advantageously used for the realization of composite electrodes to be combined with all types of electrolytes commonly used in EDLCs (see Table 1). Nevertheless, both PVdF and PTFE are rather expensive (ca. 15 € kg⁻¹, see Table 1). Moreover, while PTFE is usually used in water suspensions, PVdF requires the use of cost-expensive (and in some case toxic) organic solvents like *N*-methyl pyrrolidone (NMP).

In the last years also sodium-carboxymethyl cellulose (CMC) was proposed as binder for EDLC electrodes. CMC is environmentally more friendly (fluorine-free) and cheaper (1–2 € kg⁻¹, see Table 1) than the state-of-the-art binders. Moreover, since CMC is soluble in water, this binder allows the use of aqueous slurries for the electrode preparation, improving the overall safety of the EDLCs manufacturing process. Recent work showed that the performance of CMC-based electrodes is comparable with that of electrodes based on conventional, fluorinated binders in several types of electrolytes, both in term of capacitance and cycling stability [15–17]. However, because of the CMC solubility in water, these electrodes cannot be used in combination with aqueous electrolytes.

Natural cellulose is the most abundant natural polymer. It is a renewable, natural resource produced from organic materials like wood and cotton, and it is manufactured and regenerated in multi-ton scale every year to be used as paper, tissue paper, cellophane, etc. Cellulose is a cheap material, and its average production costs are estimated between 0.5 and 1.5 € kg⁻¹, depending on the yearly production [18]. Considering these characteristics, the introduction of cellulose as binder in EDLCs would represent an important contribution for the realization of cheap and environmentally friendly devices. However, natural cellulose cannot be dissolved in water and is also insoluble in almost all organic solvents. For this reason, it cannot be easily introduced in the electrode manufacturing process to replace state-of-the-art binders. In order to use this natural compound in composite electrodes, alternative processing methods, with respect to the conventional processes, are therefore needed.

Natural cellulose is soluble in certain ionic liquids, e.g. 1-ethyl-3-methylimidazolium acetate (EMIM Ac) [19–21, 22]. It has been recently shown that this characteristic can be successfully exploited for the realization of composite electrodes for lithium ion batteries [18]. It is important to note that this preparation method, although it involves the use of an ionic liquid, is very cost-effective and that EMIM Ac can be fully recovered [18]. Thus, the introduction of cellulose as binder for EDLCs appears possible.

In this manuscript we report the preparation of composite electrodes based on activated carbon containing natural cellulose as the binder, and their use as electrodes for EDLCs. Two different processing methods were considered. The first method was similar to the method used for the preparation of lithium-ion battery

electrodes [18]. The second method involved the use of natural cellulose in an aqueous suspension containing a polymeric stabilizer and a surfactant. In the first part of paper the thermal stability of the prepared composite electrodes, following these two methods, is reported and compared with that of conventional binders. Afterward, the electrochemical performance of the considered electrodes was investigated in aqueous, propylene carbonate and ionic liquids-based electrolytes.

2. Experimental

2.1. Electrode preparation

Composite electrodes were prepared using the activated carbon DLC Super 30 (Norit) as the active material and the carbon Super-C65 (TIMCAL) as the conductive agent using two different methods (indicated in the following pages as method A and method B).

Method A consisted in a procedure similar to that described in detail earlier [18]. Prior to the slurry preparation, the activated carbon and the conductive additive were initially dry mixed for 30 min. A 2 wt.% solution of natural cellulose, C6663-long fibers (Sigma–Aldrich), was dissolved at 60 °C in 1-ethyl-3-methylimidazolium acetate (EMIM Ac, BASF) by magnetic stirring for 30 min. Afterward, the dry mixture of the activated carbon and conductive agent was added to the binder solution and homogenized for 12 h. The slurry was cast on pre-etched aluminum foils (20 µm, purity >99.9%, etched in 5% KOH at 60 °C for 30 s) or stainless steel foil (25 µm, 18 Cr 9 Ni) by using a laboratory-scale doctor blade coater. The coated electrodes were immediately immersed in deionized water to remove the ionic liquid solvent. As the ionic liquid dissolves in the water phase, it leaves the water-insoluble cellulose behind. After immersion in water for 30 min the electrodes were dried at 60 °C under ambient atmosphere. Disk electrodes with an area of 1.13 cm² were cut out from the coated sheets and finally dried under vacuum (10⁻³ mbar) at 170 °C for 12 h. The composition of the dry electrodes was 85 wt.% activated carbon, 10 wt.% conductive agent and 5 wt.% cellulose binder. The electrode mass loading was about 2 mg cm⁻². In the following paragraph the electrodes prepared using this method will be indicated as electrodes “A”.

In method B the activated carbon and conductive agent were dry mixed for 30 min prior the slurry preparation. Natural microcrystalline cellulose (Acros Organics, average particle size 50 µm) in water (3 wt.%) was homogenized with a sonic finger in deionized water to obtain a suspension. 2 wt.% solution of polyethylene oxide (PEO, molecular weight 100.000) was dissolved in deionized water and then added to the cellulose suspension. Afterward, the dry mixture of activated carbon and conductive agent was added to the binder solution, followed by the addition of 4 wt.% of surfactant (Triton X-100). The obtained slurry was homogenized using a high-energy stirrer (5 k r.p.m.) and casted on pre-etched aluminum foils (20 µm, purity >99.9%, etched in 5% KOH at 60 °C for 30 s) or stainless steel foil (25 µm, 18 Cr 9 Ni) by using a laboratory-scale doctor blade coater. The electrodes were then dried at 60 °C under ambient atmosphere. Disk electrodes with an area of 1.13 cm² were cut out from the coated sheets and finally dried under vacuum (10⁻³ mbar) at 170 °C for 12 h. The composition of the dry electrodes was 75 wt.% activated carbon, 15 wt.% conductive agent 2 wt.% PEO and 8 wt.% cellulose binder. It is important to note that the weight of the surfactant is not considered as it decomposes during the drying step. The electrode mass loading was about 2 mg cm⁻². In the following paragraph the electrodes prepared using this method will be indicated as electrode “B”.

Table 1

Comparison of some properties of polytetrafluoroethylene (PTFE), polyvinylidene difluoride (PVdF), sodium-carboxymethyl cellulose (CMC) and natural cellulose.

Binder	Average cost/(€ kg ⁻¹)	Compatibility with		
		Aqueous electrolyte	Organic electrolyte	Ionic liquid electrolyte
PTFE	~15	Compatible	Compatible	Compatible
PVdF	~15	Compatible	Compatible	Compatible
CMC	1–2	Incompatible	Compatible	Compatible
Cellulose	0.5–1.5	Compatible	Compatible	Compatible

In order to compare the performance of the electrodes prepared using method A and B, also composite electrodes containing CMC and PVdF binder have been prepared following the procedure prior described in literature [15].

2.2. Thermal characterization

Thermogravimetric measurements were carried out using a Q5000 IR TGA instrument (TA Instruments). High-temperature platinum pans loaded with 10–20 mg samples were used for the tests. All samples were heated to 60 °C for 2 h, to remove traces water, and further up to 1000 °C with a heating rate of 5 °C min⁻¹, using nitrogen as purge gas (10 ml min⁻¹).

2.3. Electrochemical characterization

The electrodes were tested in three different kinds of electrolytes: a solution of 1 M tetraethylammonium tetrafluoroborate (Et₄NBF₄) in propylene carbonate (PC), a mixture of *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR₁₄TFSI) and PC (1:1 wt.%) and a solution of 1 M Na₂SO₄ in deionized water. For the tests carried out in 1 M Et₄NBF in PC and in the mixture PYR₁₄TFSI–PC, electrodes coated on Al-current collector were used. In case of the aqueous electrolyte, electrodes coated on stainless steel foil were used in order to prevent corrosion processes on the current collector.

Electrochemical tests were carried out in 3-electrode Swagelok®-type cells. The cells were assembled in an argon-filled glove box (H₂O <1 ppm, O₂ <1 ppm) if organic and ionic liquids-based electrolytes were used. Symmetric cells, consisting of two identical electrodes, were assembled. All cells used a Whatman GF/D glass microfiber filter discs (675 μm in thickness and 12 mm in diameter) as the separator, which was drenched with 120 μL of electrolyte solution (independent on the type of electrolyte used in the experiment).

All electrochemical tests were performed at room temperature using a VMP multichannel potentiostatic-galvanostatic system

(Biologic Science Instrument, France). Cyclic voltammetry was carried out at scan rates ranging from 5 to 200 mV s⁻¹. Galvanostatic cycling measurements were carried out using currents ranging from 5 to 20 mA cm⁻². The specific capacitance (*C*), equivalent series resistance (ESR) and efficiency (*η*) were calculated as indicated in Ref. [15]. The values of specific capacitance were always referred to the mass of the active material (activated carbon DLC Super 30, Norit).

3. Results and discussion

Fig. 1 illustrates the two preparation methods (A and B) used for the realization of the natural cellulose-based electrodes.

Method A involves the use of the ionic liquid EMIM Acetate as solvent for cellulose. As proposed by Heinze et al. cellulose dissolves in EMIM Acetate due to the formation of covalent bond between the C-1 carbon of the glucose unit and the C-2 of the imidazolium core. This dissolution can be exploited to obtain slurries containing cellulose and the electrode active materials, which can be coated over current collector for the realization of composite electrodes. In order to be used, the removal of the EMIM Acetate present on the electrodes is required. An elegant way to simultaneously remove and recover the EMIM Acetate consists in immersing the casted foil in water. As a matter of fact, upon immersion in water the bond between EMIM Acetate and cellulose is cleaved. As a consequence, the hydrophilic ionic liquid dissolves in the aqueous phase, and it can be easily recovered and recycled via distillation while the cellulose precipitates thus binding the composite electrode.

Method B involves the use of ultrasonic treatment in order to produce a homogenous dispersion of the natural cellulose in deionized water. As sedimentation of the cellulose needs to be prevented during further processing, a thickener (polyethylene oxide) is needed. Additionally, the hydrophilic polyethylene oxide chain is dissolved in water while the hydrophobic/lipophilic hydrocarbon group of the dissolved surfactant is linked to the cellulose. The stabilization via the surfactant allows a proper

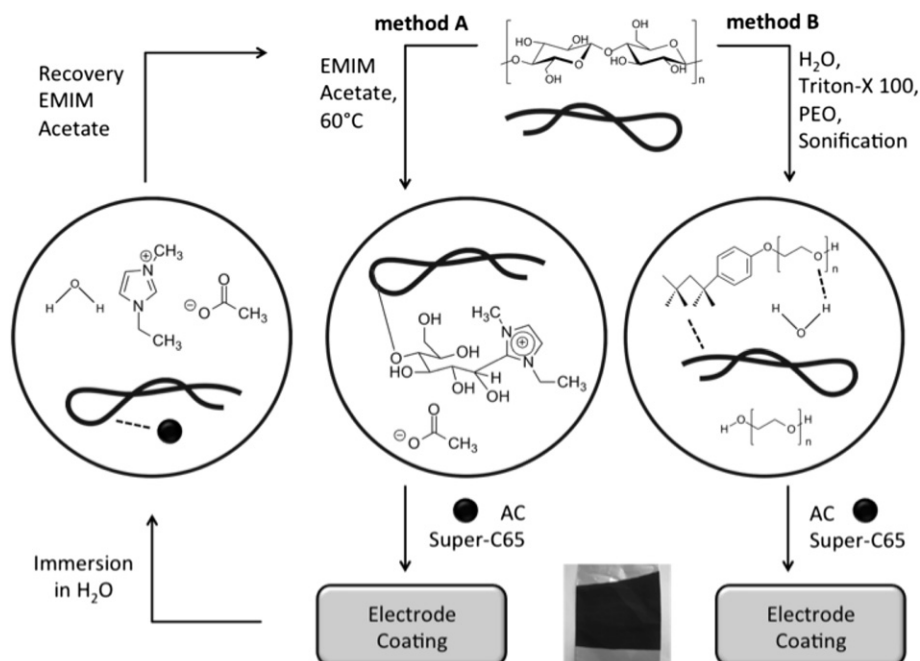


Fig. 1. Schematic representation of the electrode preparation processes via method A, including the recovery step for EMIM acetate, and B.

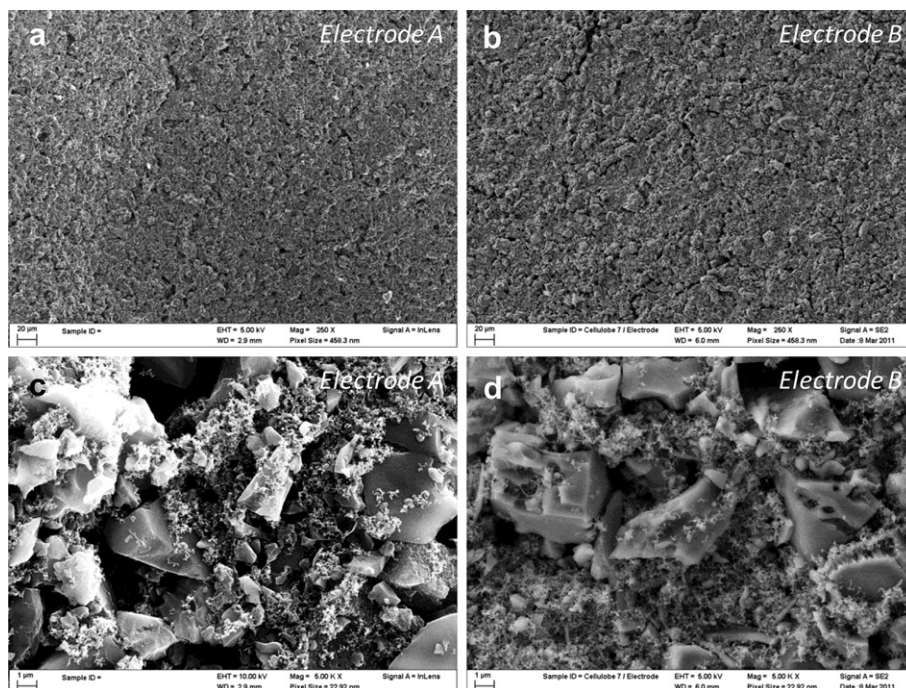


Fig. 2. SEM images of activated carbon electrodes containing natural cellulose as binder: (a, c) electrode prepared using method A; (b, d) electrode prepared using method B.

dispersion of cellulose, active material and conductive agent, resulting in the casting of high quality electrodes.

Fig. 2 shows the SEM images of electrodes A and B. As seen in the figure (Fig. 2a and c), both preparation methods lead to the realization of composite electrodes displaying a homogenous distribution of active materials and conductive agent. No aggregation of the active material particles takes place, with the conductive agent being well dispersed between the active material particles (Fig. 2b and d). Both methods appear feasible for the realization of composite electrodes of good quality, and therefore usable in EDLCs.

In Fig. 3 the TGA curves of both electrodes and natural celluloses used are depicted. The tests were performed under inert atmosphere to avoid oxidation and/or contamination with the atmosphere. All samples were preheated at 60 °C to remove residual water. As showed in Fig. 3a, electrode A displayed at 600 °C a total weight loss of about 15 wt.%, with major weight loss starting at about 300 °C. Considering that the active material and conductive

agent are known to be stable at this temperature (300 °C) [23], the major weight loss is probably determined by the binder present inside the electrode. In order to clarify this point, we investigated the thermal stability of the pure cellulose used for the electrode preparation. As shown in Fig. 3a, in the temperature range between 300 and 400 °C the natural cellulose used in electrode A loses more than 95 wt.% of its initial weight. Considering that electrode A loses about 6 wt.% of its original weight between 300 °C and 400 °C, and taking into account the binder content of electrode A (5 wt.%), the binder degradation appears effectively to be the main responsible for the weight loss observed in the electrode A.

Electrode B displays thermal stability comparable to that of electrode A, and a total weight loss of 15 wt.% in the investigated temperature range (Fig. 3b). Also in the case of this electrode, the natural cellulose used as binder was identify as the main responsible for the weight loss. As show in Fig. 3b, the natural cellulose used in electrode B lost 90% of its weight in the temperature range between 260 and 380 °C, and was almost completely decomposed

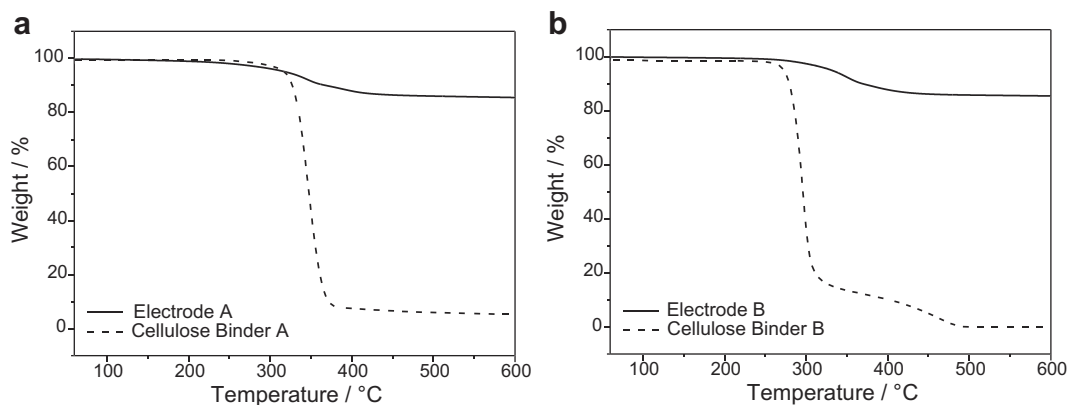


Fig. 3. (a) Thermal stability of electrode A and of the natural cellulose used as binder in this electrode and (b) thermal stability of electrode B and of the natural cellulose used as binder in this electrode.

Table 2

Comparison of thermal stability of polytetrafluoroethylene (PTFE), polyvinylidene difluoride (PVdF), sodium-carboxymethyl cellulose (CMC) and two natural celluloses (indicated as A and B).

Binder	Decomposition temperature/°C
PTFE	~300 (melting)
PVdF	~150 (melting)
CMC	~250
Cellulose A	295
Cellulose B	260

at 600 °C. This behavior is reflected in the thermal stability of electrode B. As a matter of fact, this electrode showed a weight loss of about 10 wt.% between 260 and 380 °C, which is in very good agreement with the fraction of binder (8 wt.% cellulose and 2 wt.% PEO) present in this electrode. Table 2 compares the thermal stability of the two natural celluloses used in electrodes A and B with those of PVdF, PTFE and CMC. As shown in the table, the thermal stability of the natural celluloses is comparable, or even higher, to that of the fluorinated binders PVdF and PTFE. Although these binders do not easily decompose, their temperature range of use is limited by their melting points. The considered celluloses show also higher thermal stability with respect to CMC, which starts to decompose at around 250 °C due to the release of the carboxymethyl substituents. Considering these results, the thermal stability of cellulose-based electrodes appears therefore comparable with that of electrode realized with conventional binder.

As mentioned in the Introduction, the use of cellulose as the binder in composite electrodes containing activated carbon would

be important for the development of cheap, safe and environmentally friendly EDLCs. However, in order to be very effective, the introduction of such binder cannot lead to a reduction of the EDLCs performance. With the aim to understand if the use of natural cellulose might affect the performance of these devices, we evaluated the electrochemical performance of electrodes A and B. Considering that such electrodes might be usable in all types of electrolyte, because of the insolubility of cellulose in aqueous and organic solvents, we carried out test in three different electrolytes: 1 M Et₄NBF₄ in PC, a mixture PYR₁₄TFSI–PC (1:1 wt.%), and 1 M Na₂SO₄ in H₂O.

Fig. 4 compares the CV profiles of EDLCs containing electrodes A and B in the three considered electrolytes at a scan rate of 20 mV s^{−1}. The performance in the aqueous electrolyte 1 M Na₂SO₄ in H₂O, 1 M Et₄NBF₄ in PC and PYR₁₄TFSI–PC was investigated using a cell voltage of 0.8 V, 2.5 V and 3.5 V, respectively [15,17,24]. As shown in the figure, the CV profile was influenced by the characteristics of the used electrolyte (e.g. conductivity and viscosity). However, it is important to note that both systems display the typical capacitive behavior in all electrolytes, and neither faradaic reaction nor evident decomposition processes could be observed in the CV profiles (Fig. 4a, c). The capacitance displayed by the systems in the two non-aqueous electrolytes was comparable to that showed by the same active material in CMC-based electrodes as well as in electrode containing conventional binders [15,17], indicating that the use of natural cellulose and the innovative coating process does not affect the electrode capacitance. The electrode capacitance in the aqueous electrolyte was slightly higher than that observed in PC and PC–PYR₁₄TFSI mixture, which is, most likely,

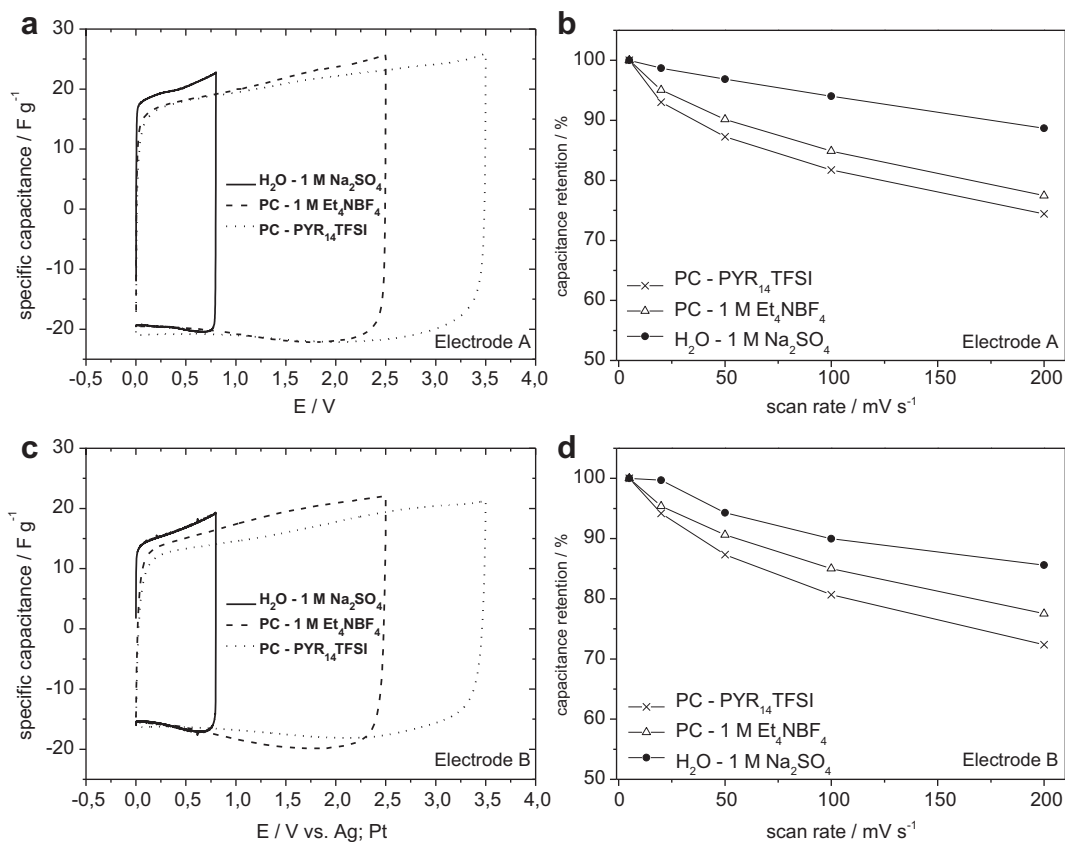


Fig. 4. Specific capacitance values of EDLC containing electrode A (a) and electrode B (c) in 1 M Na₂SO₄ in H₂O, 1 M Et₄NBF₄ in PC and PC/PYR₁₄TFSI 1:1 (wt.) mixture obtained from CVs at 20 mV s^{−1} by dividing the specific current by the scan rate. Capacitance retention of EDLCs containing electrode A (b) and electrode B (d) calculated from CVs at scan rates from 5 to 200 mV s^{−1}.

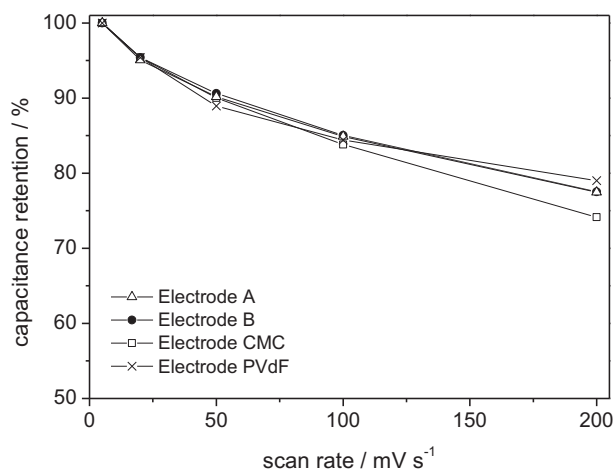


Fig. 5. Capacitance retention of EDLCs containing electrode A, electrode B, CMC-based electrode and PVdF-based electrodes calculated from CVs at scan rates ranging from 5 to 200 mV s⁻¹ carried out in 1 M Et₄NBF₄ in PC electrolyte (cell voltage 2.5 V).

due the surface chemistry of the activated carbon. However, such a difference was not so marked as for other activated carbon reported in literature [24,25]. When the scan rate was increased, the capacitance of the systems decreased, but not dramatically. At 200 mV s⁻¹ EDLCs based on both electrodes displayed more than 75% of their initial capacitance, independently on the electrolytes used. As the aqueous electrolyte features the highest conductivity as well as lowest viscosity, the capacitance retention shown by the EDLCs in this electrolyte was higher than in the other two (Fig. 4). In

aqueous electrolyte the EDLC based on electrode A displayed higher capacitance retention with respect to that of electrode B (ca. 5%). However this difference was not observed in the other electrolytes where the capacitance retention of the two EDLC was practically the same.

Fig. 5 compares the capacitance retention of the EDLC containing electrode A and B with those showed by EDLCs containing CMC and PVdF-based electrodes in the electrolyte 1 M Et₄NBF₄ in PC. As shown in the figure, the four EDLC display comparable capacitance retention for all considered scan rate, indicating that the use of natural cellulose and the innovative coating process does not negatively affect the electrode performance.

To further investigate the performance of the EDLC containing cellulose as binder, we carried out charge–discharge tests at current densities ranging from 5 to 20 mA cm⁻² in order to evaluate the coulombic efficiency, ESR and capacitance of electrodes A and B in the considered electrolytes. As shown in Fig. 6 the performance of the two electrodes was rather similar. The coulombic efficiency of the charge–discharge process was always close to 100% in both EDLCs, independent on the applied current density and the used electrolyte. However, as expected, the electrode ESR was affected by the used electrolytes, which was about of 2 Ω cm⁻² in aqueous electrolyte, 6 Ω cm⁻² in 1 M Et₄NBF₄ in PC, and 10 Ω cm⁻² in the mixture PC–PYR₁₄TFSI. These values of ESR are slightly higher than those obtained with composite electrodes containing CMC [17]. Nevertheless, considering that the preparation process can be further optimized, these values can be considered as promising. Depending on the electrolyte, the electrode capacitance ranged from 70 to 80 F g⁻¹. It is important to note that these values of capacitance are comparable with those showed by the same active material in CMC-based electrodes [15,17]. When the current density

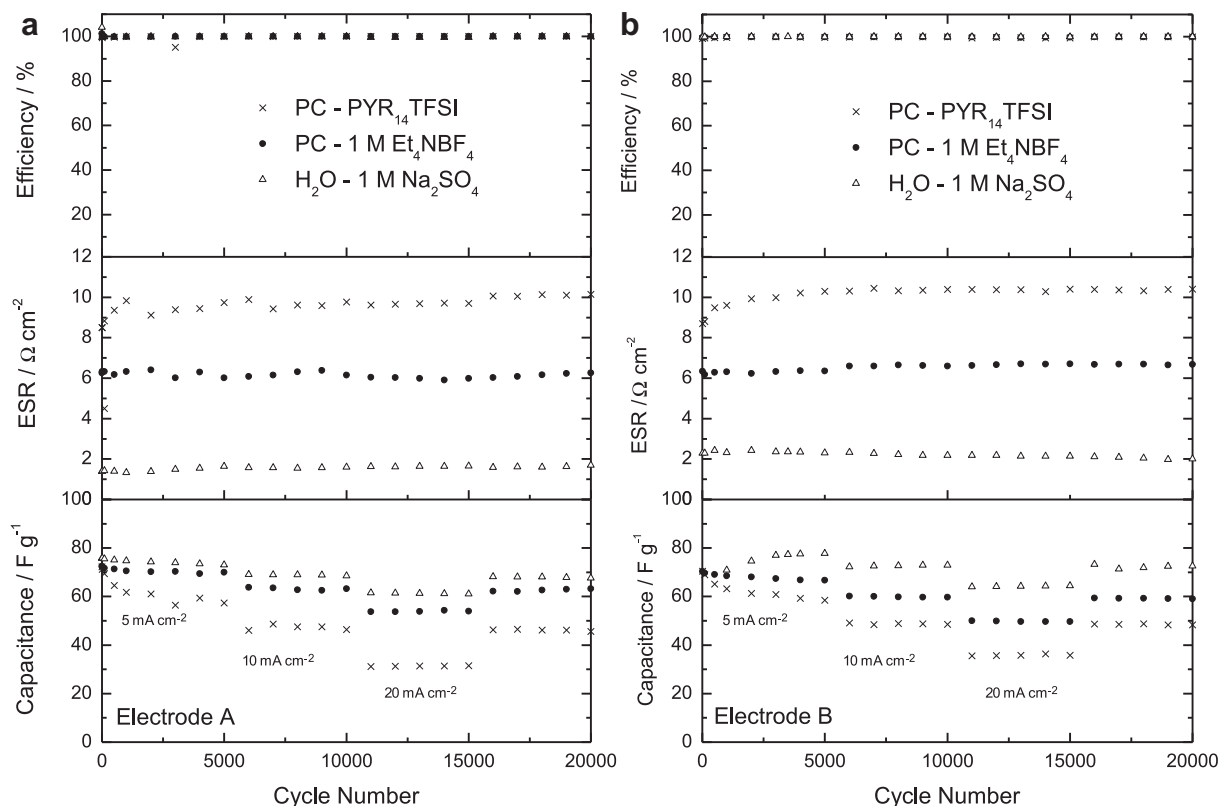


Fig. 6. Evolution of coulombic efficiency, ESR and electrode specific capacitance of the total active material vs. cycle number for EDLC containing electrode A (a) and electrode B (b) obtained from galvanostatic charge–discharge measurements at 5, 10, and 20 mA cm⁻² carried out in the electrolytes 1 M Na₂SO₄ in H₂O (cell voltage 0.8 V), 1 M Et₄NBF₄ in PC (cell voltage 2.5 V) and PC/PYR₁₄TFSI 1:1 (wt.) (cell voltage 3.5 V).

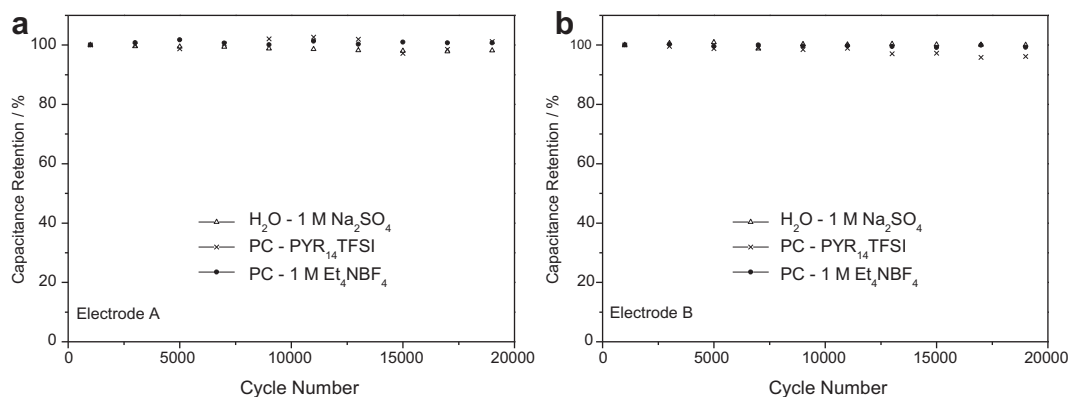


Fig. 7. Capacitance retention vs. number of cycles for EDLC containing electrode A (a) and electrode B (b) during galvanostatic charge–discharge cycles carried out at 10 mA cm^{-2} in $1 \text{ M Na}_2\text{SO}_4$ in H_2O (cell voltage 0.8 V), $1 \text{ M Et}_4\text{NBF}_4$ in PC (cell voltage 2.5 V) and PC/PYR₁₄TFSI 1:1 (wt.) (cell voltage 3.5 V).

was increased, the electrode specific capacitance decreased, but not dramatically. As expected, the higher decrease was observed in the PC–PYR₁₄TFSI, which is the electrolyte with the highest viscosity. As shown in the figure, EDLCs based on both electrodes showed a stable behavior in all electrolytes. Additionally, after the test at different current densities, the EDLCs showed performance comparable to its initial one.

With the aim to further investigate the cycling stability of the EDLCs in all three electrolytes, we finally carried out 20,000 cycles at the current density of 10 mA cm^{-2} (Fig. 7). The evaluation of the capacitance retention showed that the EDLCs display good cycling stability in all electrolytes. Even so, it is interesting to note that the two EDLCs displayed a slightly different behavior. After 20,000 cycles the EDLC containing the electrode A showed capacitance retention of about 98% in aqueous electrolyte, and capacitance retention of 100% in PC and PC–PYR₁₄TFSI. On the other hand, after the same number of cycles the EDLC containing electrode B showed capacitance retention of 100% in the aqueous electrolyte, and capacitance retention of 99% and 96% in PC and PC–PYR₁₄TFSI mixture, respectively. The different behavior of these EDLCs in the considered electrolytes was most likely related with the electrode preparation. Nevertheless, the results of these tests clearly showed that these electrodes display promising performance in terms of specific capacitance and cycling stability in different types of electrolytes.

4. Conclusion

Composite electrodes containing natural cellulose as binder and activated carbon as the active material can be prepared using either ionic liquid-based slurries or aqueous suspension containing a polymeric stabilizer and a surfactant. These composite electrodes display uniform morphology and thermal stabilities comparable to those of conventional electrodes. Moreover, when used as electrodes in EDLCs, they allow the realization of devices able to display high performance in term of specific capacitance and cycling stability in all classes of electrolytes proposed for EDLCs. The performance of these cellulose-based electrodes needs to be further improved. Nevertheless, the results of this study indicate that a natural, abundant and cheap material like natural cellulose can be successfully introduced in the manufacturing process of EDLCs. Considering the properties of natural cellulose, the introduction of this material would be an important contribution for the development of cheap, safe and environmentally friendly EDLCs.

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